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(54) **Thermowelded artikels based on polyolefin fibres**

Wärmeverschweisste Artikel auf Basis von Polyolefinfasern

Articles soudés à chaud basés sur des fibres de polyoléfines

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(56) References cited:
EP-A- 0 228 837 **EP-A- 0 276 923**
US-A- 4 222 931

• **PATENT ABSTRACTS OF JAPAN vol. 7, no. 281**
(C-200)(1426) 15 December 1983 & JP- 58 160 333
(TOA NENRYO KK) 22 September 1983

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Description

The present invention concerns thermally welded articles obtained from thermoweldable polyolefin fibres containing one or more organic phosphites and/or phosphonites, and/or HALS (Hindered Amine Light Stabilizer), and optionally small quantities of one or more phenolic antioxidants.

Within the definition of fibers are included also the manufactured products similar to fibers, such as fibrils, monofilaments, and raffia.

Polyolefin fibers are used widely in manufacturing thermally welded products, in particular of nonwoven textiles, through various technologies, the most important of which, like calendering and spun bonding, require that the fibers have the capability of thermowelding at temperatures lower than the melting point of the polyolefins which constitute them.

Moreover said fibers and manufactured articles obtained from them must be resistant to aging, yellowing, and to the color variations induced by gas fading and oxidizing phenomena in general.

Fibers obtained from polyolefins containing the most commonly used stabilizers, such as phenolic stabilizers, have little welding capability when they are submitted to a thermomechanic treatment carried out at a temperature lower than the melting point of the polyolefins.

Therefore, the mechanical properties of nonwoven textiles obtained by calendering the above mentioned fibers are poor.

In order to increase substantially the strength of thermowelding among the fibers, it has been suggested that bicomponent olefin fibers, i.e., constituted by two polyolefins, such as polypropylene and polyethylene, are used, and the one with the lowest melting temperature is the one covering the surface of the fiber.

The results obtained this way are usually poor because of incompatibility phenomena between polyolefins of a different chemical nature.

US-A-4473677 shows that the thermoweldability of polyolefins fibers can be improved by adding to the polyolefins a 3,3',4,4'-benzophenone tetracarboxylic acid di-anhydride or one of its alkyl derivatives. However, fibers thus obtained have a reduced resistance to yellowing and ageing.

EP-A-0276923 describes fibers which possess an improved ability to resist heat and discoloration, and are obtained from a polyolefin composition comprising (A) 0.05 to 1 part by weight of a hindered amine compound, (B) 0.02 to 1 part by weight of an organic phosphorus compound, and (C) 0.02 to 0.5 part by weight of hydrotalcite, said parts by weight being based on 100 parts by weight of polyolefin. The thermoweldability of said fibers is not mentioned in this document.

JP-A-58160333 (Patent Abstracts of Japan) describes a composition containing 100 parts by weight of a polyolefin (e.g. polyethylene), a hindered heterocyclic amine (0.01 to 1 part by weight) and an organic phosphite (0.01 to 1 part by weight), suitable for forming discoloration- or coloration-free moldings with improved heat resistance. Fibers are not mentioned in this document.

US-A-4222931 describes various kinds of stabilized polymer compositions, e.g. stabilized polyolefin compositions, which can be used to produce fibers having better resistance to discoloration and embrittlement on ageing and heating. Said compositions contain 2,6,6,6-tetramethyl-4-piperidyl carboxylic acid ether or ether alcohol (from about 0.01 to about 5%), a phenolic antioxidant (from about 0.001 to about 5%), a phosphonate ester (from about 0.001 to about 5%) and optionally a phosphite. The thermoweldability of the fibers is not mentioned in this document.

However, fibers obtained this way have a reduced resistance to yellowing and aging.

Unexpectedly, the Applicant found that thermowelded articles obtainable from polyolefin fibers with high thermoweldability, resistant to aging, yellowing, and color variations due to "gas fading" and oxidizing processes, can be obtained by starting with olefin crystalline polymers containing one or more of the following stabilizers:

- a) from 0.01 to 0.5%, preferably from 0.05 to 0.15% by weight of one or more organic phosphites and/or phosphonites;
- b) from 0.005 to 0.5%, preferably from 0.01 to 0.025% by weight of one or more HALS;

and optionally one or more phenolic anti-oxidants in concentration not exceeding 0.02% by weight.

Said olefin polymers can be in granular or nonextruded particle form, having geometrically regular form, such as flakes or spheroidal particles.

The stabilizers are incorporated during the extrusion and granulation phase of the particles, or the nonextruded particles are coated or impregnated with the stabilizers at least on the surface, preferably after the polymerization stage.

The coating or impregnation of the nonextruded particles, particularly the spheroidal particles having diameters preferably between 0.5 and 4.5 mm, can be done in a variety of ways, such as, for example, the treatment with solution or suspension of the stabilizers and an optional subsequent evaporation of the solvent or suspension medium.

Alternately, in the processes for extrusion spinning described below, the particles of polymer mixed with the above-

mentioned stabilizers can be introduced directly into the extruder.

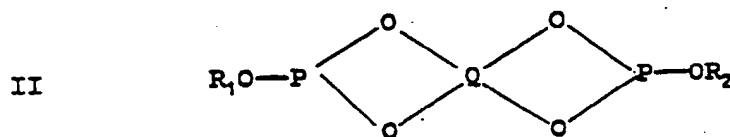
In general the additivated polyolefins used to prepare the manufactured articles according to the present invention have a melt flow index, determined according to ASTM D 1238-L regulation, between 0.5 and 100 g/10 minutes, more preferably between 1.5 and 35 g/10 minutes, obtained directly in polymerization or through controlled radical degradation.

In order to obtain the controlled radical degradation, organic peroxides are added during the granulation phase or directly in the fibers' extrusion phase.

The organic phosphites that can be used as additives for polyolefins used according to the present invention are preferably selected among compounds with the following general formulas:

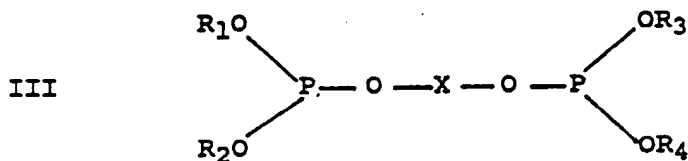


where R_1 , R_2 , R_3 , equal or different, are alkyl, aryl, or arylalkyl radicals having 1-18 carbon atoms:



where R_1 and R_2 , equal or different, are radicals having the above-mentioned meaning;

Q is a tetravalent alkyl radical;



where R_1 , R_2 , R_3 , R_4 , equal or different, are radicals having the significance already indicated for radicals R, X is a bivalent alkyl, aryl, or arylalkyl radical.

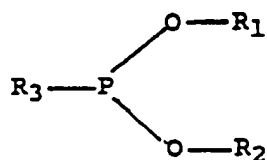
Examples of organic phosphites comprised in the general formula I are described in US Patents No. 4,187,212 and No. 4,290,941, which are incorporated herein for reference.

Specific examples of compounds included in general formulas I, II, III are:

tris(2,4-di-ter-butylphenyl)phosphite sold by CIBA GEIGY under the Irgafos 168 trademark; distearyl pentaerythritol diphosphite sold by BORG-WARNER CHEMICAL under the Weston 618 trademark; 4,4'-butylidenebis(3-methyl-6-ter-butylphenyl-ditridecyl)phosphite sold by ADEKA ARGUS CHEMICAL under the Mark P trademark; tris(monononylphenyl)phosphite; bis(2,4-di-ter-butyl)pentaerythritol diphosphite, sold by BORG-WARNER CHEMICAL under the Ultrinox 626 trademark.

The organic phosphonites that can be used as additives according to the present invention are preferably selected among the compounds of general formula:

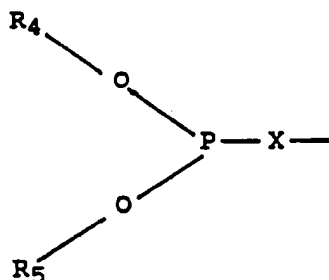
IV



where R_1 , R_2 , R_3 , equal or different, are alkyl, aryl, or arylalkyl radicals having 1-18 carbon atoms.

Alternatively, and this is preferred, the R_3 radical can be substituted by a group

V



where R_4 and R_5 , equal or different, are radicals having the above indicated significance for the R radicals, and X is a bivalent alkyl, aryl, or arylalkyl radical.

Examples of organic phosphonites included in general formula IV, which can conveniently be used according to the present invention, are described in GB patent No. 1,372,528 which is incorporated herein for reference.

A preferred example of compounds comprised in general formula IV is the tetrakis(2,4-di-ter-butylphenyl)4,4'-diphenylenediphosphonite, sold by Sandoz under the Sandostab P-EPQ trademark.

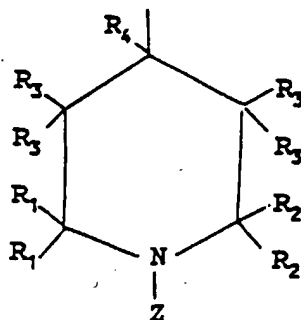
The organic phosphites and phosphonites are generally used to inhibit degradation and oxidation of polyolefins in the molten state (process stabilizers), and therefore, according to known state of the art, require the addition of high quantities of phenolic stabilizers to obtain a complete stabilization.

The HALS, which according to the present invention are also used as polyolefins stabilizers, are amine compounds with steric hindrance of the aminic function, which are generally used as stabilizers for polyolefins in the solid state against oxidation induced by light.

In this case as well, according to known state of the art, the addition of a high quantity of phenolic stabilizers is necessary for a satisfactory stabilization of polyolefin manufactured articles.

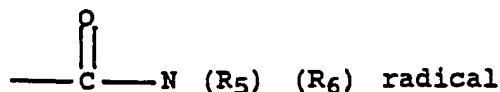
The HALS used according to the present invention are monomeric or oligomeric compounds containing, in the molecule, one or more substituted piperidine groups having the following general formula:

VI



where the R_1 radicals, equal or different, are C_1 - C_4 alkyl radicals, or tetramethylpiperidine radicals, or the alkyl radicals form with the piperidine carbon atoms to which they are linked a C_5 - C_9 cycloalkyl radical; the R_2 radicals, equal or different, are hydrogen or C_1 - C_{18} alkyl radicals, C_7 - C_{18} arylalkyl radicals, or the alkyl radical form with the piperidine

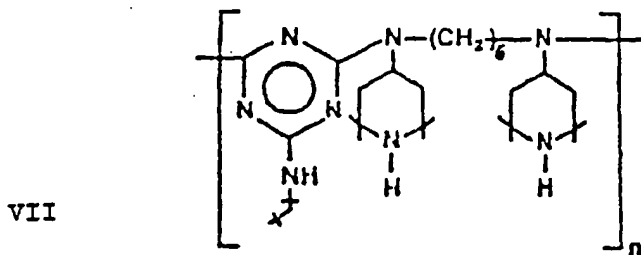
carbon atoms to which they are linked a C₅-C₁₀ cycloalkyl radical; the R₃ radicals, equal or different, are hydrogen, or C₁-C₁₈ alkyl radicals or C₇-C₁₈ arylalkyl radicals; the R₄ radical is hydrogen, or a C₁-C₈ alkyl radical, or a benzyl radical; Z is hydrogen, or a C₁-C₁₈ alkyl, C₁-C₁₂ alkylene, C₃-C₁₂ alkenyl, C₃-C₆ alkynyl, C₇-C₁₈ arylalkyl, C₂-C₄ acyl, C₂-C₁₈ alkanoyl, C₃-C₁₈ alkoxyalkyl, C₃-C₁₈ alkenoyl, oxylic, cyanomethyl, xylylenyl radical, or a radical having a 1 to 4 valence and containing from 1 to 4 hydroxyl groups and, optionally, ether, ester, or heterocyclic groups, being the valences of said radical linked to the nitrogen of piperidine groups, or a bivalent radical containing one or more ester or amide groups, or a



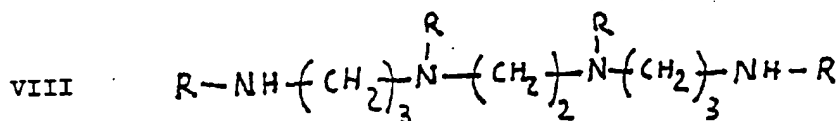
where R₅ and R₆ are hydrocarbon radicals.

Preferably Z is a C₁-C₁₂ alkyl radical, or a C₃-C₈ alkenyl, C₇-C₁₁ aralkyl radical, or a bivalent radical containing one or more ester groups, being the valences of said radicals linked to the nitrogen atom of piperidine groups.

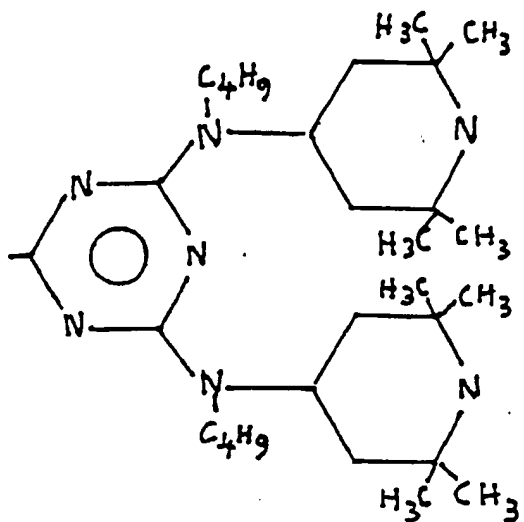
Specific examples of preferred HALS according to the present invention are compounds having the following formula:



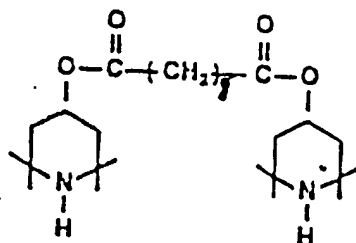
where n generally varies from 2 to 20. A compound of this type is sold by CIBA-GEIGY with the Chimassorb 944 trademark.



sold by CIBA-GEIGY under the Chimassorb 905 trademark, where R is:

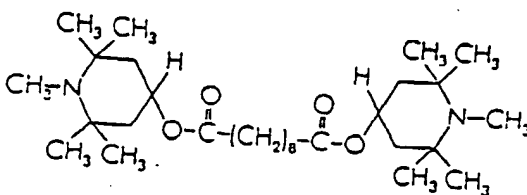


IX



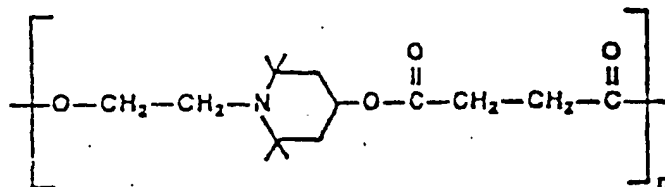
sold by CIBA-GEIGY under the Tinuvin 770 trademark.

X



sold by CIBA-GEIGY under the Tinuvin 292 trademark

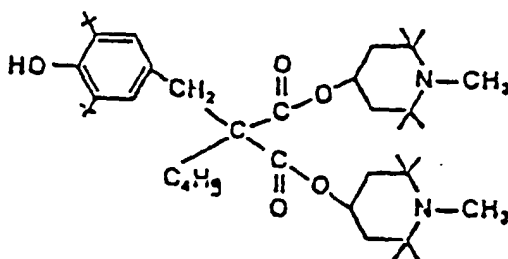
XI



where n generally varies from 2 to 20.

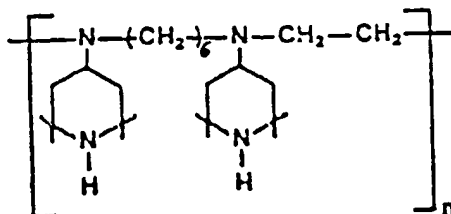
A compound of this type is sold by CIBA-GEIGY under the Tinuvin 622 trademark.

XII



sold by CIBA-GEIGY under the Tinuvin 144 trademark.

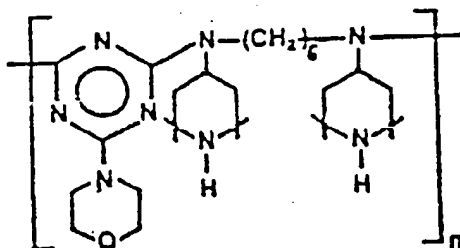
XIII



where n generally varies from 2 to 20.

A compound of this type is sold by CIBA-GEIGY under the Spinuvex A36 trademark.

XIV



where n generally varies from 2 to 20.

A compound of this type is sold by AM.CYANAMIDE under the Cyasorb UV 3346 trademark.

As previously said, in addition to the above-mentioned additives, optionally, one or more phenolic antioxidants (sterically hindered phenols) can be used in concentration not higher than 0.02% by weight.

Examples of preferred phenolic antioxidants are: tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4,6-(1H, 3H, 5H)trione, sold by CYANAMID under the Cyanox 1790 trademark; calcium bis[monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate]; 1,3,5-tris (3,5-di-tert-butyl-4-hydroxybenzyl)-s-triazine-2,4,6-(1H,3H,5H) trione; 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl)benzene; pentaerythritol-tetrakis[3(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], sold by CIBA-GEIGY under the following trademarks: Irganox 1425, Irganox 3114; Irganox 1330; Irganox 1010; 2,6-dimethyl-3-hydroxy-4-tert-butyl benzyl abietate.

The additives commonly used to stabilize polyolefins, particularly Ca, Mg, Zn stearates, can also be used in the preparation of the fibers according to the invention.

The polyolefins which can be used in the present invention comprise crystalline polymers or copolymers, or their mixtures, of olefins of the R-CH-CH₂ formula where R is a hydrogen atom or a C₁-C₆ alkyl radical.

Particularly used are:

- 1) isotactic or prevailing isotactic polypropylene;
- 2) HDPE, LLDPE, LDPE polyethylene;
- 3) crystalline copolymers of propylene with ethylene and/or other alpha-olefins, such as for instance 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, where the total comonomer content varies from 0.05% to 20% by weight;
- 4) heterophasic polymers constituted by (A) a homopolymer fraction of propylene or one of the copolymers mentioned in item (3), and a copolymer fraction (B) made up by ethylene-propylene or ethylene-propylene-diene rubber copolymers. Said heterophasic polymers being prepared according to known methods via mixing in the melted state of the above-mentioned components, or sequential copolymerization, and containing the copolymer fraction (B) in quantities from 5% to 80% by weight, and the polypropylene fraction in quantities from 20% to 80% by weight;
- 5) syndiotactic polypropylene and its random or heterophasic copolymers as described in items (3) and (4).

Preferably used are isotactic or prevailing isotactic polypropylene, and propylene-ethylene crystalline copolymers with a prevalent propylene content.

In order to obtain thermowelded articles obtained from polyolefin fibers according to the present invention, any spinning process and apparatus for melt extrusion known in the field may be used.

For the preparation of the fibers it's preferable to use extruders with spinners' holes having a length/diameter ratio greater than 2.

The operation can occur at a spinner's temperature between 260°C and 300°C, and at a spinning velocity between 0.1 and 0.8 g/min hole.

During the spinning it's possible to introduce in the fibers other additives such as pigments, opacifiers, fillers, etc.

The fibers obtained by extrusion are eventually submitted to stretching with stretching ratios generally between 1:1.1 and 1:8 and at temperatures between 80°C and 150°C, preferably between 100° and 130°C, using stretching apparatus heated, i.e., with hot air, vapor, or heating plates.

The melt flow index of the fibers obtained in this manner is usually higher with respect to the values of the original polyolefins because of the spinning treatment.

Indicatively, one can obtain melt flow index values for the fibers between 4 and 150 g/10 minutes.

The fibers obtained with the above-mentioned methods can be mono- or multifilament, and may be used for the preparation of staples or thermally cohered products, especially of nonwoven textiles.

Optionally, before the transformation to finished manufactured articles, the fibers can be submitted to refinishing treatments such as crimp, thermofixing, etc.

As previously stated, the nonwoven textiles may be prepared with a variety of known technologies, such as the calendering of staple fibers and the spun bonding, operating preferably at a temperature of 10-20°C lower than the melt temperature of the polyolefins constituting the fibers.

Said products have high mechanical properties, thanks to the mechanical resistance of the thermowelding that can be obtained with the fibers of the present invention.

The above-mentioned fibers, in fact, are characterized by a high thermowelding strength, determined according to the method described in the examples. Preferably this parameter varies from 2 to 5 N.

Moreover, the manufactured articles derived from the fibers of the present invention show satisfactory resistance to aging and color changes.

EXAMPLES

EVALUATION OF THE PROPERTIES OF THE FIBERS PREPARED IN THE EXAMPLES

THERMOWELDING STRENGTH

Usually, in order to evaluate the thermowelding ability of the fibers it is customary to produce a nonwoven via calendering under special conditions, and measure the stress necessary to tear said nonwoven in a direction transversal to the calendering one, operating according to ASTM 1682 regulation.

The stress value determined in this manner is considered a measure of the ability of the fiber to thermoweld.

The result obtained, however, is influenced substantially by the finishing characteristics of the fibers (crim, finish, thermofixing, etc.) and the condition of preparation of the card veil fed to the calender.

In order to prevent these inconveniences and obtain a more direct evaluation of the thermowelding characteristics of the fibers, a method has been devised which will be schematically described below.

Some samples are prepared starting with a rove of 400 tex (ASTM D 1577-7 regulation) and 0.4 m long, made up of continuous fibers.

After having twisted said rove eighty times, the two extremities are joined, obtaining a manufactured article where the two halves of the rove are twisted around each other as in a rope.

The two twisted roves are thermowelded at a temperature of about 15°C lower than the melting point of the polyolefin which makes up the fibers, operating for a predetermined period of time with a thermowelder of the type commonly used in laboratories for the study of thermoplastic films.

The average force required to detach the two roves of each sample at the thermowelded point is measured with a dynamometer.

The result, expressed in N, is obtained by averaging out at least 8 measurements, and it expresses the thermowelding strength among fibers.

In the following examples a Sentinel model 12-12 AS thermowelder was used, operating with thermowelding periods of 1 second and a thermowelding pressure of about 2.85 Kg/cm².

COLOR CHANGES

The IXSO/TC38/SC1 norm was used at 60°C and at 130°C to measure the resistance of fibers to colorations induced by gas fading, while the resistance to colorations induced by oxidation phenomena was measured by keeping the fibers in an oven at 90°C for 2 days, and the coloration was evaluated based on the gray scale, as described in the above-mentioned norm.

RESISTANCE TO ARTIFICIAL AGING

The above-mentioned property was evaluated by submitting the fibers to accelerated aging in a ventilated oven at 110°C, according to ASTM D 3045-74 regulation.

The time (in days) necessary to reach total decay of the mechanical properties (embrittlement) was determined.

EXAMPLES 1-14 AND COMPARATIVE EXAMPLES 1-8

We prepared 5 Kg. samples made up of polypropylene in flake form at controlled granulometry (average diameter of particles 450 m) with the following characteristics:

- residue insoluble in boiling heptane 96%
- number average molecular weight 65,700
- weight average molecular weight 320,000
- melt flow index 12.2 g/10 min
- ashes at 800°C 160 ppm

and additivated with calcium stearate at a concentration of 0.05% by weight.

To each sample were added the stabilizers listed in Table 1, through a Henschell type speed mixer for powders.

The mixture thus obtained have been granulated by extrusion at 220°C, and the granules have been spun in a system with the following main characteristics:

- extruder with 25 mm diameter screw and length/diameter ratio = 25, and a capacity from 1.0 to 6.0 Kg/h;
- spinner with 19 holes with a diameter of 0.4 mm and length/diameter ratio = 5;
- metering pump;
- quenching system with air at a temperature of 18-20°C;
- gathering device with a speed of 500 to 2000 m/min.;
- fiber stretching device with hot roller at speed varying from 30 to 300 m/min, and steam stretch oven.

The conditions used for spinning and stretching were:

- a) temperature of spinner = 290°C;

b) hole capacity 0.45 g/min.;

c) gathering speed 1500 m/min;

d) stretch ratio 1:1.5.

The main mechanical characteristics of the fibers thus obtained are included in the following ranges:

- titre (ASTM D 1577-79 regulation) 1.9 - 2.2 dtex
- strenght (ASTM D 2101-82 regulation) 15-20 cN/tex
- elongation to break (ASTM D 2101-82 regulation) 300-400%.

In table 1 are shown for all the examples the thermowelding strength (thermowelding temperature = 150°C), the accelerated aging resistance values (in days), and the color changes compared to the gray scale.

In particular, for the color changes, the first result reported in Table 1 is relative to the change induced by gas fading at 60°C after 4 cycles, the second result is relative to the change induced by gas fading at 130°C after 15 minutes, the third to the coloration induced by oxidizing phenomena, determined as described above.

EXAMPLES 15-17 and COMPARATIVE EXAMPLE 9

5 Kg. samples have been prepared, made up of polypropylene in the form of spheroidal particles with diameter between 2 and 3 mm and having the following characteristics:

- insoluble in xylene at 25°C 96.5%
- number average molecular weight 64,000
- weight average molecular weight 325,000
- melt flow index 11.8 g/10 min.
- ashes at 800°C 150 ppm

The above-mentioned samples have been surface additivated with the stabilizers shown in Table 2.

The additivation was done by treatment with aqueous suspensions and subsequent drying. The polymer particles have then been further additivated with calcium stearate in weight concentration of 0.05%.

The polymer thus obtained was spun according to methods described in preceding examples.

The mechanical properties of the fibers were within the ranges described in the preceding examples.

In Table 2 are shown, for all examples, the thermowelding strength (thermowelding temperature = 150°C), the accelerated aging resistance values in days, and color changes, determined as per the preceding examples.

EXAMPLE 18

5 Kg of random crystalline propylene/ethylene copolymer containing 2.3% by weight of ethylene, are additivated with:

- 0.05% by weight calcium stearate;
- 0.05% by weight of Sandostab P-EPQ;
- 0.01% by weight of Chimassorb 944;

and then they are granulated by extrusion.

The methods employed are the same as described in examples 1-14.

The granules are then spun with the same technologies described in example 1-14.

The mechanical properties of the fibers thus obtained were within the ranges described in examples above-men-

tioned.

The thermowelding strength (thermowelding temperature = 140°C) was 3.8 N.

The time of resistance to accelerated aging and the color changes, measured as described above, were respectively 6 and 5 days; 5; 5.

EXAMPLES 19-23

Operating in the same conditions and same propylene homopolymer of examples 1-14, we prepared samples in the form of extruded granules containing the following additives (percentage by weight):

- 0.05% calcium stearate
- 0.015% Chimassorb 944
- 0.04% Irgafos 168
- 0.01% Irganox 1076.

The granules were spun with the same methods of examples 1-14 using the gathering speed and the stretching ratios indicated in Table 3 for each example.

In the same table are also shown the title, strength, and elongation at break values of the fibers obtained, as well as the thermowelding strength (thermowelding temperature = 150°C), resistance to aging and color change values, determined as per the preceding examples.

Table 1

Example No.	Additives	% by weight	Thermowelding strength N	Accelerated aging days	Colour change
1	Weston 610	0.05%	2.5	2.0	5; 5; 5
2	Sandostab P-EPQ	0.05%	2.0	2.0	5; 5; 5
3	Irgafos 168	0.05%	3.0	2.0	5; 5; 5
4	Chimassorb 944	0.02%	3.0	4.0	5; 5; 5
5	Chimassorb 944	0.05%	3.0	6.0	5; 5; 5
6	Tinuvin 622	0.02%	3.0	4.0	5; 5; 5
7	Tinuvin 770	0.02%	3.0	4.0	5; 5; 5
8	Tinuvin 144	0.02%	3.0	4.0	5; 5; 5
9	Tinuvin 144 Chimassorb 905	0.05% 0.02%	3.0	5.0	5; 5; 5
10	Sandostab P-EPQ Chimassorb 944	0.05% 0.02%	3.5	6.0	5; 5; 5
11	Irgafos 168 Chimassorb 944	0.05% 0.02%	4.0	6.0	5; 5; 5
12	Irgafos 168 Chimassorb 944	0.05% 0.05%	4.2	10	5; 5; 5
13	Tinuvin 622 Irgafos 168	0.02% 0.05%	4.0	6.0	5; 5; 5

continued: Table 1

Example No.	Additives	% by weight	Thermowelding strength N	Accelerated aging days	Colour change
14	{ Sandostab PEPQ Tinuvin 144	0.05% 0.02%	3.5	6.0	5; 5; 5
Comparative					
Example No.					
1	Irganox 1010	0.05%	1.2	2.0	2; 2; 2
2	Irganox 1425	0.05%	1.4	4.0	3; 3; 3
3	Irganox 3114	0.05%	1.5	2.0	4; 3; 3
4	Cyanox 1790	0.05%	1.5	3.0	4; 3; 2
5	{ Irganox 1010 Irgafos 168	0.05% 0.05%	1.0	2.0	2; 2; 2
6	{ Irganox 1010 Chimassorb 944	0.05% 0.05%	1.0	10	2; 2; 2
7	Tinuvin 622	0.8%	1.8	15	4; 4; 4
8	{ Tinuvin 622 Sandostab P-EPQ	0.8% 0.7%	2.5	20	4; 4; 5

Table 2

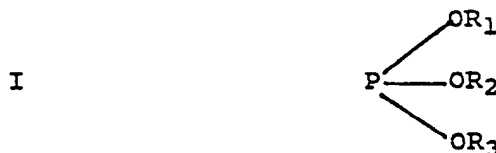
Example No.	Additives	% by weight	Thermowelding strength	Accelerated aging days	Colour change
15	Chlmassorb 944	0.02%	4.0	6	5; 5; 5
	Irgafos 168	0.05%			
16	Sandostab P-EPQ	0.05%	3.0	2	5; 5; 5
17	Tinuvin 144	0.02%	3.8	6	5; 5; 5
	Irgafos 168	0.05%			
Comparative Example No.					
9	Irganox 1010	0.05%	1.2	2	2; 2; 2

Table 3

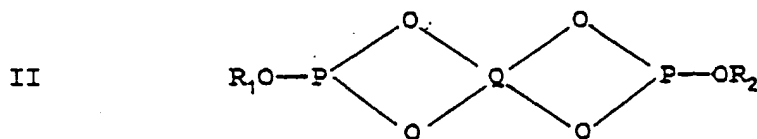
Example No.	Gathering speed m/min.	Stretching ratio	Title dtex	Strength	Elongation at break %	Thermowelding strength N	Accelerated aging days	Colour change
19	2000	1 : 1.25	1.9	15	400	3.2	5	5; 5; 5
20	1500	1 : 1.7	2.1	18	350	3.1	5	5; 5; 5
21	1000	1 : 2.5	2.0	24	280	3.3	6	5; 5; 5
22	800	1 : 3.1	1.95	27	200	3.1	6	5; 5; 5
23	600	1 : 4.1	2.2	32	100	3.0	5	5; 5; 5

Claims

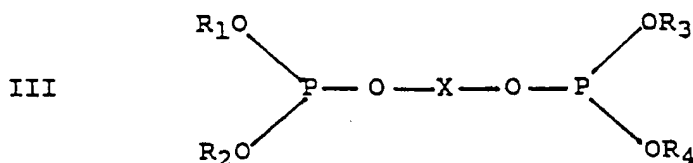
1. Thermally welded manufactured articles obtainable from thermoweldable polyolefin fibers comprising an olefin crystalline polymer containing as stabilizer(s), based on the total weight of the olefin crystalline polymer and stabilizer(s):
 - a) from 0.01 to 0.5% by weight of one or more organic phosphites and/or phosphonites, and/or;
 - b) from 0.005% to 0.5% by weight of one or more HALS, wherein any phenolic antioxidant is either absent or present in concentration not greater than 0.02% by weight, the thermowelding being carried out by operating at a temperature lower than the melt temperature of the polyolefin constituting the fibers.
2. Thermally welded manufactured articles according to claim 1 in the form of nonwoven textiles obtained by calendaring or spun bonding the fibers described in claim 1.
3. Thermally welded manufactured articles according to claim 1 and 2, wherein the polymer is a homopolymer or copolymer of an olefin of the formula $R-CH=CH_2$, where R is a hydrogen atom or a C_1-C_6 alkyl radical.
4. Thermally welded manufactured articles according to claim 3, wherein the polymer is selected from isotactic, or prevailing isotactic polypropylene, and propylene-ethylene crystalline copolymers containing prevalently propylene.
5. Thermally welded manufactured articles according to claim 1 and 2, wherein the stabilizer(s) (a) content varies from 0.05 to 0.15% by weight, and the stabilizers (b) content varies from 0.01 to 0.025% by weight.
6. Thermally welded manufactured articles according to claims 1 and 2, wherein the organic phosphite or phosphites are selected among compounds having the general formulas:



where R_1 , R_2 , R_3 , equal or different, are alkyl, aryl, or arylalkyl radicals with 1 to 18 carbon atoms:

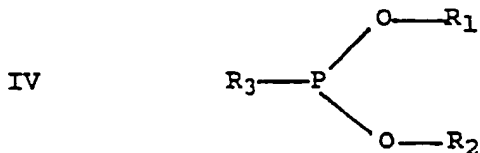


where R_1 and R_2 , equal or different, are radicals having the above-mentioned meaning; Q is a tetravalent alkyl radical;

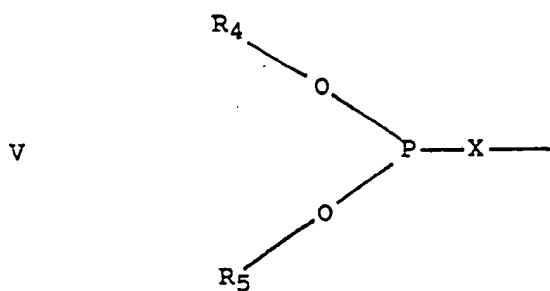


where R_1 , R_2 , R_3 , R_4 , equal or different, are radicals with the meaning indicated for the R radicals, X is an alkyl, aryl, or arylalkyl bivalent radical.

7. Thermally welded manufactured articles according to claim 6, wherein the organic phosphite or phosphites are selected among tris(2,4 di-ter-butylphenyl)phosphite; distearyl pentaerythritol diphosphite; 4,4'-butylidene-bis(3-methyl-6-ter-butylphenyl-di-tridecyl)phosphite; tris(mononylphenyl)phosphite; bis(2,4-di-ter-butyl)pentaerythritol diphosphite.
8. Thermally welded manufactured articles according to claims 1 and 2, wherein the organic phosphonite or phosphonites are selected among compounds of the general formula:

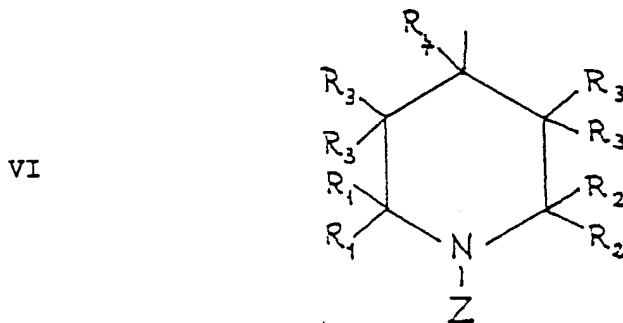


where R_1 , R_2 , R_3 , equal or different, are alkyl, aryl, or arylalkyl radicals with 1 to 18 carbon atoms, or the R_2 radical is substituted by a group

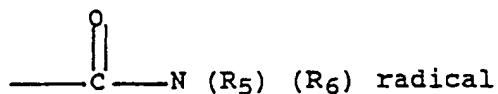


where R_4 and R_5 , equal or different, are radicals with the meaning above indicated for the R radicals, and X is an alkyl, aryl, or arylalkyl bivalent radical.

9. Thermally welded manufactured articles according to claim 8, wherein tetrakis[2,4-di-ter-butylphenyl]4,4'-diphenyl phosphonite is used as the organic phosphonite.
10. Thermally welded manufactured articles according to claims 1 and 2, wherein the HALS are selected among monomer or oligomer compounds which contain in the molecule one or more substituted piperidine groups having the following general formula:

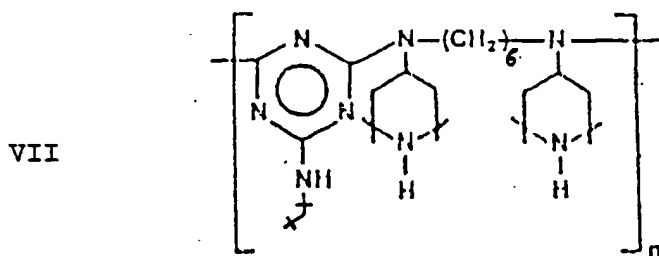


where the R_1 radicals, equal or different, are C_1 - C_4 alkyl radicals, or tetramethylpiperidine radicals, or the alkyl radicals form with the piperidine carbon atoms to which they are linked a C_5 - C_9 cycloalkyl radical; the R_2 radicals, equal or different, are hydrogen or C_1 - C_{18} alkyl radicals, C_7 - C_{18} arylalkyl radicals, or the alkyl radical form with the piperidine carbon atoms to which they are linked a C_5 - C_{10} cycloalkyl radical; the R_3 radicals, equal or different, are hydrogen, or C_1 - C_{18} alkyl radicals or C_7 - C_{18} arylalkyl radicals; the R_4 radical is hydrogen, or a C_1 - C_8 alkyl radical, or a benzyl radical; Z is hydrogen, or a C_1 - C_{18} alkyl, C_1 - C_{12} alkylene, C_3 - C_{12} alkenyl, C_3 - C_5 alkynyl, C_7 - C_{18} arylalkyl, C_2 - C_4 acyl, C_2 - C_{18} alkanoyl, C_3 - C_{18} alkoxyalkyl, C_3 - C_{18} alkenoyl, oxylic, cyanomethyl, xilylenyl radical, or a radical having a 1 to 4 valence and containing from 1 to 4 hydroxyl groups and, optionally, ether, ester, or heterocyclic groups, being the valences of said radical linked to the nitrogen of piperidine groups, or a bivalent radical containing one or more ester or amide groups, or a



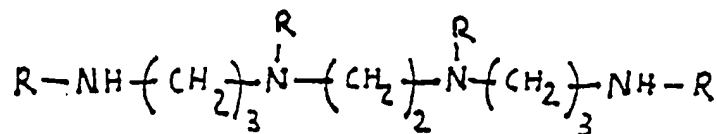
where R_5 and R_6 are hydrocarbon radicals.

11. Thermally welded manufactured articles according to claim 10, wherein the HALS is or are selected among the compounds with the formulas:

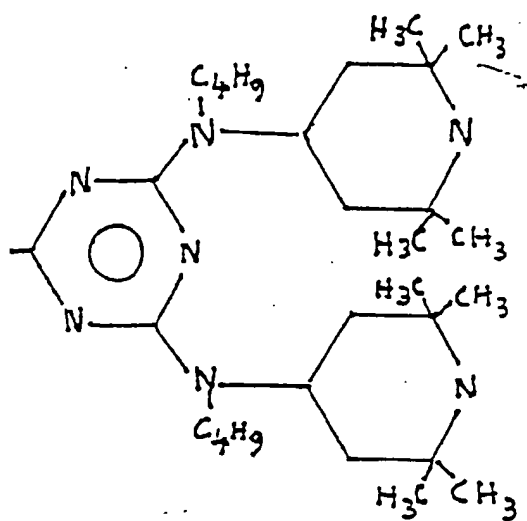


where n varies from 2 to 20.

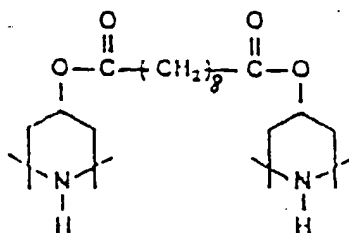
VIII



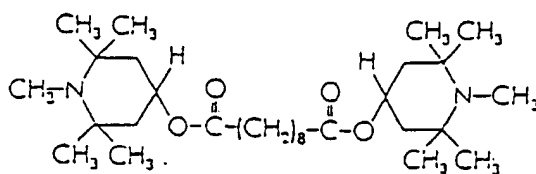
where R is:



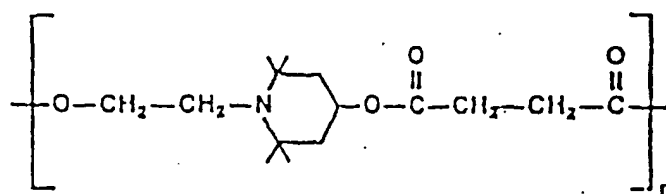
IX



X

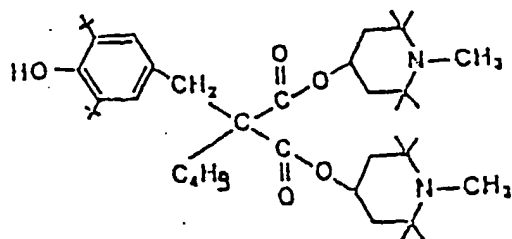


XI

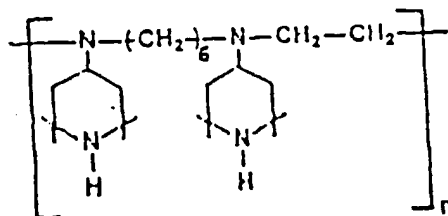


where n varies from 2 to 20.

XII

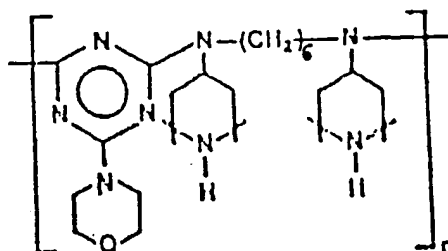


XIII



where n varies from 2 to 20.

XIV



where n varies from 2 to 20.

12. Thermally welded manufactured articles according to claims 1 and 2, wherein the phenolic antioxidant or antioxidants are selected among tris(4-*t*-butyl-3-hydroxy-2,6-dimethylbenzyl)-*s*-triazine-2,4,6-(1*H*,3*H*,5*H*)trione; calcium bi[monoethyl(3,5-di-*ter*-butyl-4-hydroxybenzyl)phosphonate]; 1,3,5-tris (3,5-di-*ter*-butyl-4-hydroxybenzyl)-*s*-triazine-2,4,6-(1*H*,3*H*,5*H*)trione; 1,3,5-trimethyl-2,4,6-tris(3,5-di-*ter*-butyl-4 butyl-4-hydroxybenzyl)benzene; pentaerythritol-tetrakis[3-(3,5-di-*ter*-butyl-4-hydroxyphenyl)propionate]; 2,6-dimethyl-3-hydroxy-4-*ter*-butyl benzyl abietate.

13. Thermally welded manufactured articles according to claims 1 and 2, having a thermoweldable strength from 2 to 4.5 N.

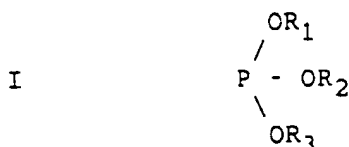
Patentansprüche

1. Wärmeverschweißte hergestellte Gegenstände, erhältlich aus wärmeverschweißbaren Polyolefinfasern, die ein kristallines Olefinpolymer umfassen, das als Stabilisator(en), basierend auf dem Gesamtgewicht von kristallinem

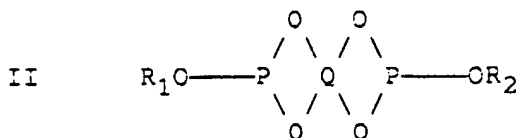
Olefinpolymer und Stabilisator(en), enthält:

- a) 0,01 bis 0,5 Gew.-% ein oder mehrere organische Phosphite und/oder Phosphonite und/oder
 b) 0,005% bis 0,5 Gew.-% einen oder mehrere HALS, worin ein phenolisches Antioxidans entweder nicht
 vorliegt oder in einer Konzentration nicht höher als 0,02 Gew.-% vorliegt, wobei das Wärmeverschweißen
 durch Arbeiten bei einer Temperatur geringer als die Schmelztemperatur des Polyolefins, aus dem die Fasern
 bestehen, ausgeführt wird.

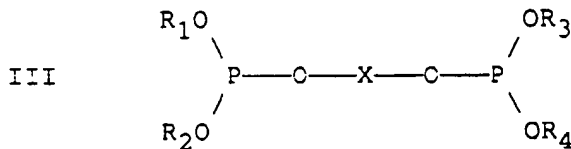
2. Wärmeverschweißt hergestellte Gegenstände nach Anspruch 1 in Vliesform, erhalten durch Kalandrieren oder
 Spunbonding der in Anspruch 1 beschriebenen Fasern.
3. Wärmeverschweißt hergestellte Gegenstände nach Anspruch 1 und 2, wobei das Polymer ein Homopolymer oder
 Copolymer eines Olefins der Formel $R-CH=CH_2$ bedeutet, worin R ein Wasserstoffatom oder einen C_1-C_6 -Alkylrest
 darstellt.
4. Wärmeverschweißt hergestellte Gegenstände nach Anspruch 3, wobei das Polymer ausgewählt ist aus isotakti-
 schem oder überwiegend isotaktischem Polypropylen und kristallinen Propylen-Ethylen-Copolymeren, die vorwie-
 gend Propylen enthalten.
5. Wärmeverschweißt hergestellte Gegenstände nach Anspruch 1 und 2, wobei der Anteil an Stabilisator(en) (a) 0,05
 bis 0,15 Gew.-% ist und der Anteil an Stabilisator(en) (b) 0,01 bis 0,025 Gew.-% ist.
6. Wärmeverschweißt hergestellte Gegenstände nach Ansprüchen 1 und 2, wobei das organische Phosphit oder die
 organischen Phosphite ausgewählt sind aus Verbindungen der allgemeinen Formeln:



worin R_1, R_2, R_3 gleich oder verschieden Alkyl-, Aryl- oder Arylalkylreste mit 1 bis 18 Kohlenstoffatomen darstellen:



worin R_1 und R_2 gleich oder verschieden Reste mit der vorstehend erwähnten Bedeutung sind; Q einen vierwer-
 tigen Alkylrest darstellt;

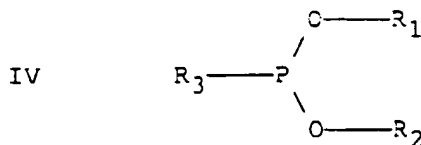


worin R_1, R_2, R_3, R_4 gleich oder verschieden Reste mit der vorstehend für die Reste R ausgewiesenen Bedeutung
 darstellen, X einen zweiwertigen Alkyl-, Aryl- oder Arylalkylrest darstellt.

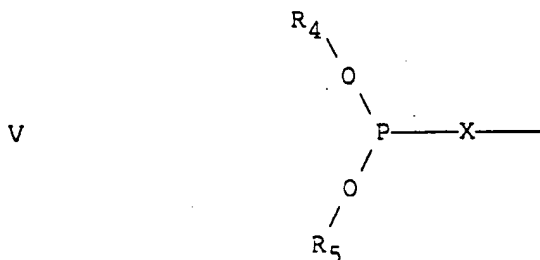
7. Wärmeverschweißt hergestellte Gegenstände nach Anspruch 6, wobei das organische Phosphit oder die organi-
 schen Phosphite ausgewählt ist/sind aus Tris(2,4-di-tert-butylphenyl)phosphiz, Distearylpentaerythritdiphosphit,

4,4'-Butyridenbis(3-methyl-6-tert-butylphenyl-di-tridecyl)phosphit, Tris-(monononylphenyl)phosphit, Bis(2,4-di-tert-butyl)pentaerythridiphosphit.

8. Wärmeverschleiß hergestellte Gegenstände nach Ansprüchen 1 und 2, wobei das organische Phosphonit oder die organischen Phosphonite ausgewählt sind aus Verbindungen der allgemeinen Formel:



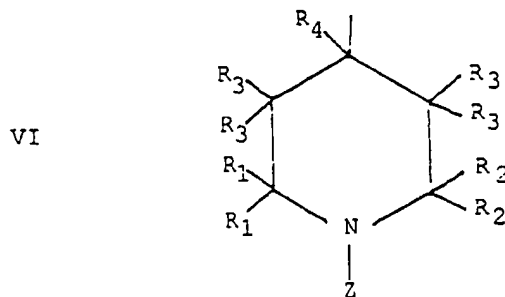
worin R_1 , R_2 , R_3 gleich oder verschieden Alkyl-, Aryl- oder Aralkylreste mit 1 bis 18 Kohlenstoffatomen darstellen oder der Rest R_3 substituiert ist mit einer Gruppe



worin R_4 und R_5 gleich oder verschieden Reste mit der vorstehend für die Reste R ausgewiesenen Bedeutung darstellen und X einen zweiwertigen Alkyl-, Aryl- oder Arylalkylrest darstellt.

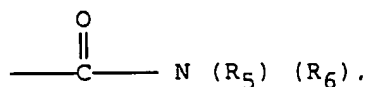
9. Wärmeverschleiß hergestellte Gegenstände nach Anspruch 8, wobei Tetrakis[2,4-di-tert-butylphenyl]4,4'-diphenylphosphonit als organisches Phosphonit verwendet wird.

10. Wärmeverschleiß hergestellte Gegenstände nach Ansprüchen 1 und 2, wobei der HALS ausgewählt ist aus Monomer- oder Oligomerverbindungen, die in dem Molekül eine oder mehrere substituierte Piperidingruppen enthalten, mit der nachstehenden allgemeinen Formel:



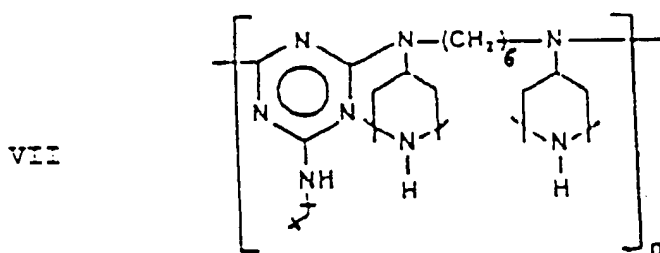
worin die Reste R_1 gleich oder verschieden C_1 - C_4 -Alkylreste oder Tetramethylpiperidinreste darstellen oder die Alkylreste mit den Piperidinkohlenstoffatomen, an die sie gebunden sind, einen C_5 - C_9 -Cycloalkylrest bilden; die Reste R_2 gleich oder verschieden Wasserstoff oder C_1 - C_{18} -Alkylreste, C_7 - C_{18} -Arylalkylreste darstellen oder der Alkylrest mit den Piperidinkohlenstoffatomen, an die sie gebunden sind, einen C_5 - C_{10} -Cycloalkylrest bilden; die Reste R_3 gleich oder verschieden Wasserstoff oder C_1 - C_{18} -Alkylreste oder C_7 - C_{18} -Aryl-alkylreste darstellen; der Rest R_4 Wasserstoff oder einen C_1 - C_8 -Alkylrest oder einen Benzylrest darstellt; Z Wasserstoff oder einen C_1 - C_{18} -

Alkyl-, C₁-C₁₂-Alkyl-, C₃-C₁₂-Alkenyl-, C₃-C₅-Alkynyl-, C₇-C₁₈-Arylalkyl-, C₂-C₄-Acyl-, C₂-C₁₈-Alkanoyl-, C₃-C₁₈-Alkoxyalkyl-, C₃-C₁₈-Alkenoyl-, Oxy-, Cyanomethyl-, Xylylenylrest oder einen Rest mit 1 bis 4 Bindungen und enthaltend 1 bis 4 Hydroxylgruppen und gegebenenfalls Ether, Ester oder heterocyclische Gruppen, wobei die Bindungen des Restes an das Stickstoffatom der Piperidingruppen gebunden sind oder einen zweiwertigen Rest, enthaltend einen oder mehrere Ester- oder Amidgruppen oder einen Rest



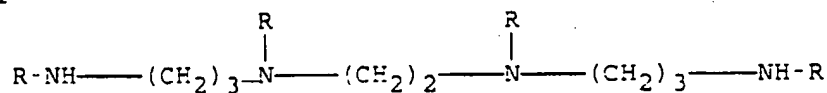
worin R₅ und R₆ Kohlenwasserstoffreste darstellen, darstellt.

11. Wärmeverschleißt hergestellte Gegenstände nach Anspruch 10, worin der/die HALS ausgewählt ist oder sind aus den Verbindungen der Formeln:

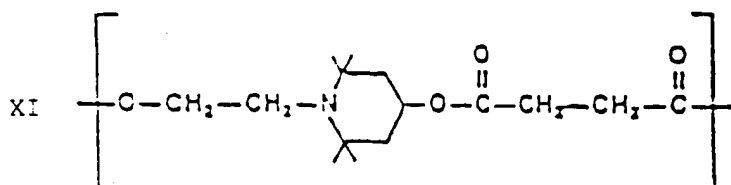
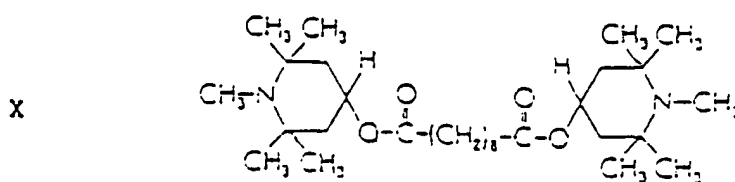
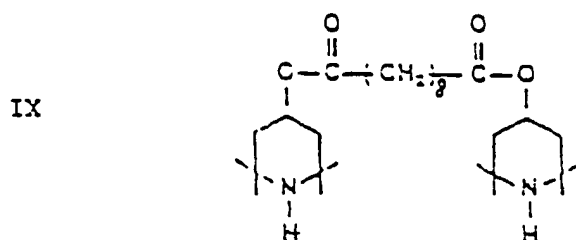
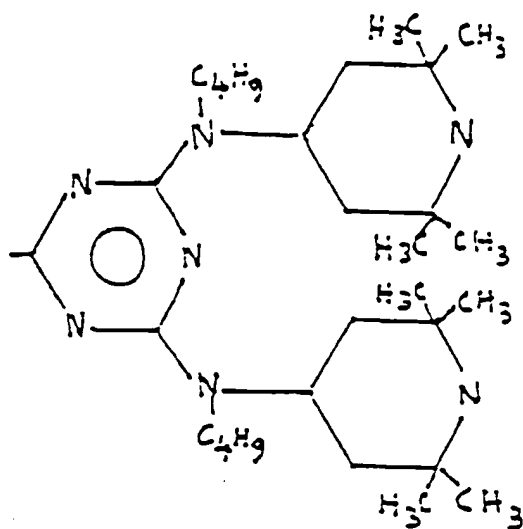


worin n von 2 bis 20 schwankt.

VIII

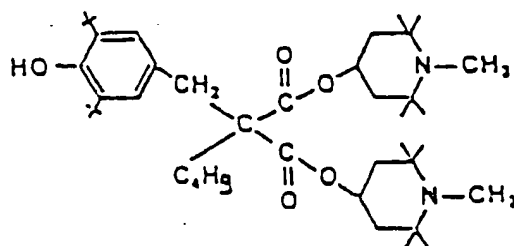


worin R ist:

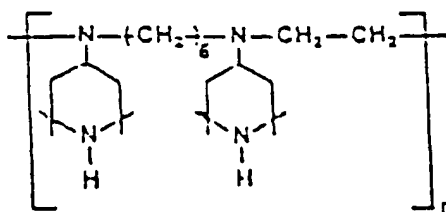


worin n von 2 bis 20 schwankt.

XII

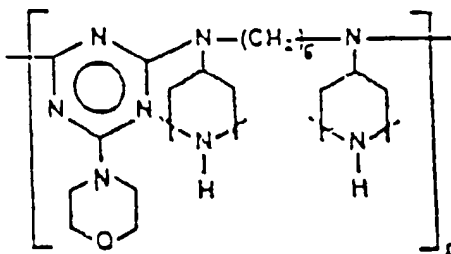


XIII



worin n von 2 bis 20 schwankt.

XIV



worin n von 2 bis 20 schwankt.

12. Wärmeverschweißte hergestellte Gegenstände nach Ansprüchen 1 und 2, wobei das/die phenolische(n) Antioxidans oder Antioxidantien ausgewählt ist/sind aus Tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazin-2,4,6-(1H,3H,5H)trion; Calcium-bis[monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonat]; 1,3,5-Tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-s-triazin-2,4,6-(1H,3H,5H)trion; 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)benzol; Pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionat]; 2,6-Dimethyl-3-hydroxy-4-tert-butylbenzylacetat.

13. Wärmeverschweißte hergestellte Gegenstände nach Ansprüchen 1 und 2, mit einer thermoverschweißbaren Festigkeit von 2 bis 4,5N.

Revendications

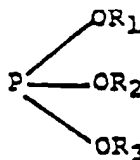
1. Articles manufacturés soudés thermiquement, susceptible d'être obtenus à partir de fibres de polyoléfine thermosoudables, comprenant un polymère cristallin d'oléfine contenant en tant que stabilisant(s), exprimés par rapport au poids total de polymère cristallin d'oléfine et de stabilisant(s):

- a) de 0,01 à 0,5% en poids d'un ou plusieurs phosphites et/ou phosphonites organiques, et/ou;
- b) de 0,005% à 0,5% en poids d'un ou plusieurs HALS,

dans lesquels tout antioxydant phénolique est soit absent, soit présent en une concentration ne dépassant pas 0,02% en poids, le thermosoudage étant effectué en opérant à une température inférieure à la température de fusion de la polyoléfine constitutive des fibres.

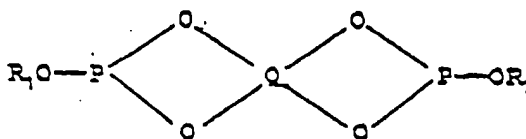
2. Articles manufacturés soudés thermiquement selon la revendication 1, sous forme de textiles non tissés, obtenus par calandrage ou entrelaçage des fibres selon la revendication 1.
3. Articles manufacturés soudés thermiquement, selon les revendications 1 et 2, dans lesquels le polymère est un homopolymère ou copolymère d'une oléfine de formule $R-CH=CH_2$, où R est un atome d'hydrogène ou un radical alkyl en C_1-C_6 .
4. Articles manufacturés soudés thermiquement selon la revendication 3, où le polymère est choisi parmi le propylène isotactique ou principalement isotactique, et les copolymères cristallins propylène-éthylène contenant principalement du polypropylène.
5. Articles manufacturés soudés thermiquement selon les revendications 1 et 2, dans lesquels la teneur en stabilisants (a) est de 0,05 à 0,15% en poids, et la teneur en stabilisants (b) est de 0,01 à 0,025% en poids.
6. Articles manufacturés soudés thermiquement selon l'une quelconque des revendications 1 ou 2, dans lesquels le ou les phosphites organiques sont choisis parmi les composés répondant aux formules générale:

I



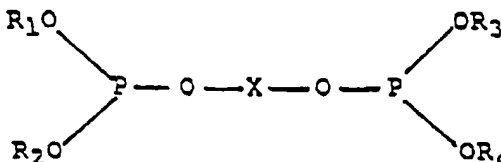
où R_1, R_2, R_3 , identiques ou différents, sont des radicaux alkyl, aryl, ou arylalkyl, comportant 1 à 18 atomes de carbone;

II



où R_1 et R_2 , identiques ou différents, sont des radicaux ayant la signification indiquée ci-dessus; Q est un radical alkyl tétravalent:

III

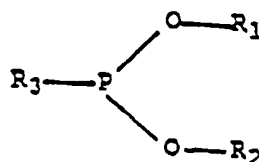


où R_1, R_2, R_3, R_4 , identiques ou différents sont des radicaux ayant la signification indiquée à propos des radicaux R, X est un radical alkyl, aryl, ou arylalkyl bivalent.

7. Articles manufacturés soudés thermiquement selon la revendication 6, dans lesquels le ou les phosphites organiques sont choisis parmi tris(2,4 di-tert-butylphényl)-phosphite; distéaryl pentaérythritol diphosphite; 4,4'-butylidène-bis(3-méthyl-6-tert-butylphényl-di-tridécyl)phosphite; tris(mononyl-phényl)phosphite; bis(2,4-di-ter-butyl)pentaérythritol diphosphite.

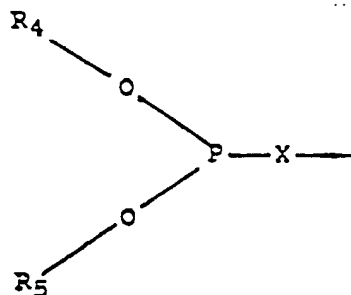
8. Articles manufacturés soudés thermiquement selon les revendications 1 et 2, dans lesquels le ou les phosphonites organiques sont choisis parmi les composés de formule générale:

IV



où R_1 , R_2 , R_3 , identiques ou différents sont des radicaux alkyl, aryl ou arylalkyl comportant 1 à 18 atomes de carbone, ou bien le radical R_2 est substitué par un groupe

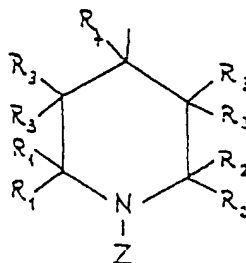
V



où R_4 et R_5 , identiques ou différents, sont des radicaux ayant la signification donnée ci-dessus pour les radicaux R_1 , et X est un radical alkyl, aryl, ou arylalkyl bivalent.

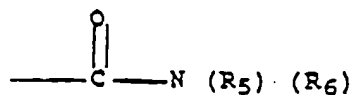
9. Articles manufacturés soudés thermiquement selon la revendication 8, dans lesquels on utilise du tétrakis[2,4-ditert-butylphényl]4,4'-diphényl phosphonite en tant que phosphonite organique.
10. Articles manufacturés soudés thermiquement selon les revendications 1 et 2, dans lesquels les HALS sont choisis parmi les composés monomères ou oligomères qui contiennent dans leur molécule un ou plusieurs groupes pipéridine substitués, répondant à la formule générale suivante:

VI



dans laquelle les radicaux R_1 , identiques ou différents, sont des radicaux alkyl en $\text{C}_1\text{-C}_4$, ou les radicaux tétraméthylpipéridine, ou les radicaux alkyl forment avec les atomes de carbone de la pipéridine auxquels ils sont rattachés un radical cycloalkyl en $\text{C}_5\text{-C}_9$; les radicaux R_2 , identiques ou différents, sont des hydrogènes ou des radicaux alkyl en $\text{C}_1\text{-C}_{18}$, des radicaux arylalkyl en $\text{C}_7\text{-C}_{18}$, ou bien le radical alkyl forme avec les atomes de carbone de la pipéridine auxquels ils sont attachés un radical cycloalkyl en $\text{C}_5\text{-C}_{10}$; les radicaux R_3 , identiques ou différents, sont des hydrogènes ou des radicaux alkyl en $\text{C}_1\text{-C}_{18}$, ou des radicaux arylalkyl en $\text{C}_7\text{-C}_{18}$, le radical R_4 est un hydrogène, ou un radical alkyl en $\text{C}_1\text{-C}_8$, ou un radical benzyl; Z est un hydrogène, ou un radical alkyl en $\text{C}_1\text{-C}_{18}$, alkylène en $\text{C}_1\text{-C}_{12}$, alkényl en $\text{C}_3\text{-C}_{12}$, alkynyl en $\text{C}_3\text{-C}_5$, arylalkyl en $\text{C}_7\text{-C}_{18}$, acyl en $\text{C}_2\text{-C}_4$, alcanoyl en $\text{C}_2\text{-C}_{18}$, alcoxyalkyl en $\text{C}_3\text{-C}_{18}$, alcénoyl en $\text{C}_3\text{-C}_{18}$, oxylique, cyanométhyl, un radical xylylényl, ou un radical comportant 1 à 4 valences, et contenant de 1 à 4 groupes hydroxyle et, le cas échéant, des groupes éther, ester et hétérocycliques, les valences dudit radical étant liées à l'azote du groupe pipéridine, ou un radical bivalent contenant un

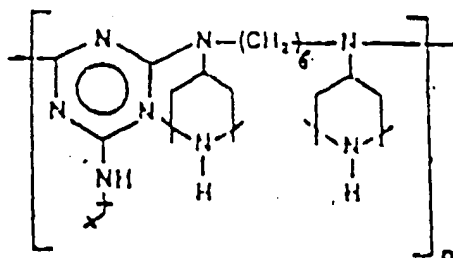
plusieurs groupes ester ou amide, ou bien un radical



où R_5 et R_6 sont des radicaux hydrocarbonés.

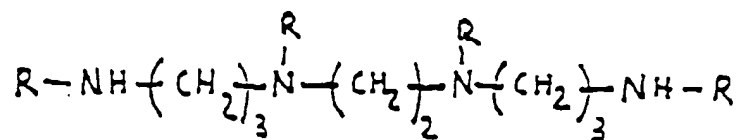
11. Articles manufacturés soudés thermiquement selon la revendication 10, dans lesquels le(s) HALS est ou sont choisis parmi les composés de formules:

VII

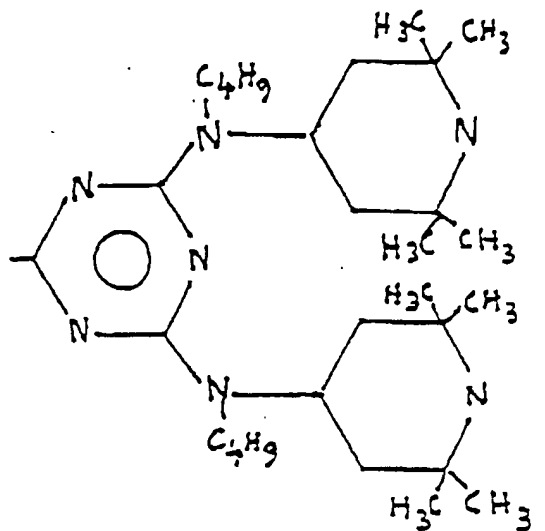


où n varie de 2 à 20.

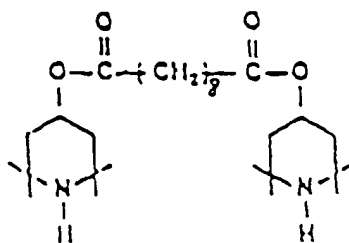
VIII



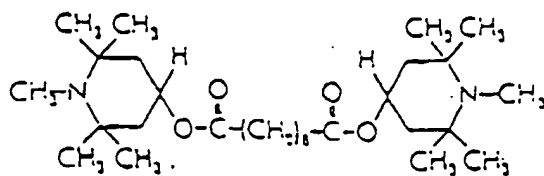
où R est



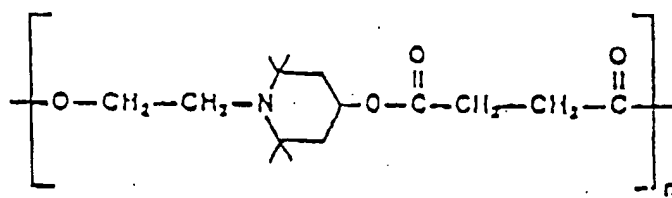
IX



X

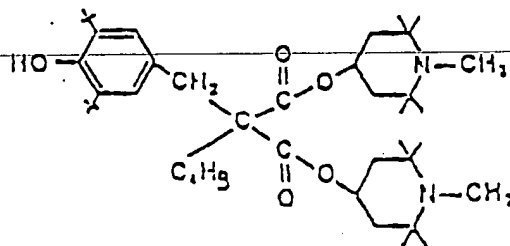


XI

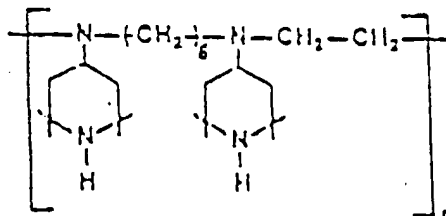


où n varie de 2 à 20.

XII

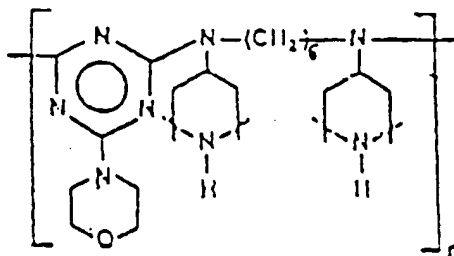


XIII



où n varie de 2 à 20,

XIV



où n varie de 2 à 20.

12. Articles manufacturés soudés thermiquement selon les revendications 1 et 2, dans lesquels le ou les antioxydant (s) phénolique(s) sont choisis parmi tris(4-*t*-butyl-3-hydroxy-2,6-diméthylbenzyl)-*s*-triazine-2,4,6-(1H,3H,5H)trione; bi[mono-éthyl(3,5-di-*ter*-butyl-4-hydroxybenzyl)phosphonate] de calcium; 1,3,5-tris(3,5-di-*ter*-butyl-4-hydroxybenzyl)-*s*-triazine-2,4,6-(1H,3H,5H)trione; 1,3,5-triméthyl-2,4,6-tris(3,5-di-*ter*-butyl-4-hydroxybenzyl)benzène; pentaérythritol-tétrakis[3-(3,5-di-*ter*-butyl-4-hydroxyphényl)propionate]; 2,6-diméthyl-3-hydroxy-4-*ter*-butyl benzyl abiétate.
13. Articles manufacturés soudés thermiquement, selon les revendications 1 et 2, avant une résistance de la thermosoudure de 2 à 4,5N.